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DIASTEREODSELECTION AND THE INFLUENCE OF CHIRAPHOS ON
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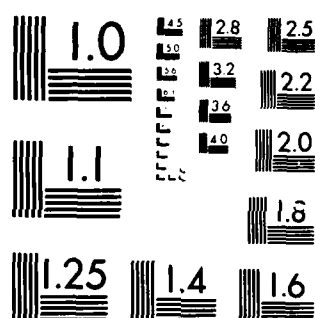
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Diastereoselection and the Influence of Chiraphos on Metal-Centered Chirality
in Cis Oxidative Addition of Hydrogen and Triphenylsilane

by

Amanda J. Kunin, Ramy Farid, Curtis E. Johnson and Richard Eisenberg*

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University of Rochester

Department of Chemistry

Rochester, NY 14627

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17. KEY WORDS (Continue on reverse side if necessary and identify by block number): Oxidative addition; Stereoselectivity; H₂ activation; silane; iridium; chirality

18. ABSTRACT (Continue on reverse side if necessary and identify by block number): The complex IrBr(CO)(chiraphos), chiraphos = 2S,2S-bis(diphenylphosphino)butane, has been prepared, and its oxidative addition reactions with H₂ and PhSiH₃ have been studied. The reaction with H₂ proceeds under kinetic control forming an initial pair of diastereomers in a 2:1 ratio followed by isomerization to a second, more stable pair of diastereomers which commence to form in a 2.4:1 ratio but exist at equilibrium in a 1.3:1 ratio. The kinetic differentiation observed for each pair of diastereomers results from the influence of chiraphos on the developing chirality at the metal center as the cis oxidative addition

proceeds. A reaction coordinate diagram for the system is developed based on the observed kinetic and thermodynamic differentiations of the diastereomers. The oxidative addition of PhSiH₃ also takes place under kinetic control followed by isomerization. A 12:1 kinetic differentiation in the formation of the stable silyl hydride diastereomers occurs at 25° C due solely to the presence of chiraphos.

Diastereoselection and the Influence of Chiraphos on Metal-Centered Chirality
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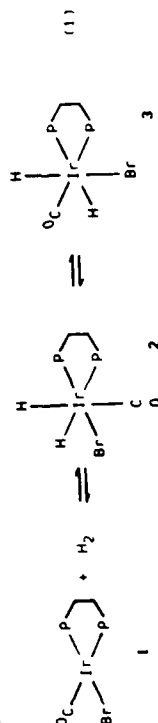
Amenda J. Kunin, Romy Farid, Curt's E. Johnson, and Richard Eisenberg
Department of Chemistry
University of Rochester
Rochester, New York 14627

Received

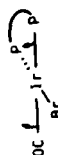
Abstract: The complex $\text{IrBr}(\text{CO})(\text{chiraphos})$, chiraphos = 2*S*,3*S*-bis-(diphenylphosphino)butane, has been prepared, and its oxidative addition reactions with H_2 and Ph_3SiH have been studied. The reaction with H_2 proceeds under kinetic control forming an initial pair of diastereomers in a 2:1 ratio followed by isomerization to a second, more stable pair of diastereomers which commence to form in a 2.4:1 ratio but exist at equilibrium in a 1.3:1 ratio. The kinetic differentiation observed for each pair of diastereomers results from the influence of chiraphos on the developing chirality at the metal center as the *cis* oxidative addition proceeds. A reaction coordinate diagram for the system is developed based on the observed kinetic and thermodynamic differentiations of the diastereomers. The oxidative addition of Ph_3SiH also takes place under kinetic control followed by isomerization. A 12:1 kinetic differentiation in the formation of the stable silyl hydride diastereomers occurs at 25°C due solely to the presence of chiraphos.

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In the stereoselective, kinetically controlled oxidative addition of H_2 to $\text{IrBr}(\text{CO})(\text{dppe})$, 1, (dppe = bis(diphenylphosphino)ethane),¹ both the kinetic isomer 2 and the thermodynamic isomer 3 form as racemates resulting from H_2 approach to the metal center from above and below the $\text{Ir}(\text{I})$ square planar complex. This is illustrated for 2 as a and b with H_2 aligned parallel



to the $\text{P}-\text{Ir}-\text{CO}$ axis of complex 1; formation of 3 proceeds similarly with H_2 parallel to $\text{P}-\text{Ir}-\text{X}$. In this communication, we describe studies in which the



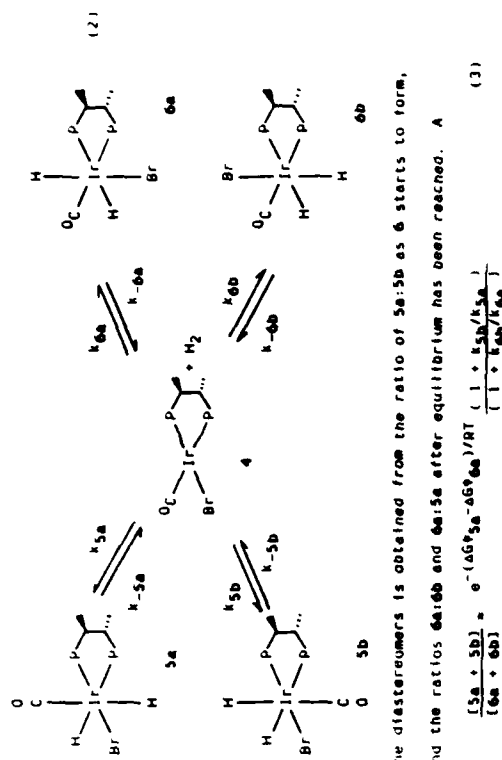
optically active diphosphine chiraphos, (2*S*,3*S*-bis(diphenylphosphino)butane),² is used in place of dppe leading to kinetic and thermodynamic differentiation of the racemic products of H_2 and Ph_3SiH oxidative addition. While the use of chiral diphosphines as catalysts for asymmetric hydrogenation has been widely investigated,^{3,4} the present work represents the first study in which the effect of chiraphos on simple oxidative addition has been examined.

The complex $\text{IrBr}(\text{CO})(\text{chiraphos})$, 4, prepared analogously to 1,^{1a} reacts with H_2 in acetone similarly to eqn (1) forming first diastereomers 5a and 5b with >99.5% stereoselectivity followed by slower formation of the more stable pair of diastereomers 6a and 6b. Figure 1 shows the hydride region of the ^1H NMR spectrum upon initial oxidative addition and subsequent isomerization, and NMR data for the diastereomers are summarized below.⁵ At -25°C, the kinetic diastereomers 5 form in a 2.1:1 ratio which remains constant for extended

periods of time, but on warming to room temperature, changes within 5 min to 1:1 as the thermodynamic diastereomers **6** start to grow in. The isomerization of **5** to **6** follows first order kinetics with a rate constant for the disappearance of **5a** at 35°C of $4.9 \times 10^{-5} \text{ s}^{-1}$. During early stages of the isomerization the observed ratio of **6a:6b** is 2.4:1, while at equilibrium the ratio is 1.3:1 with diastereomers **6** comprising 85% of the total hydride species present. At equilibrium, the ratio of **6a:5a** is 7.2:1.

To establish that the initial ratio of 2.1:1 seen for **5** at -25°C corresponds to kinetic differentiation of the diastereomers, **5** was formed at low temperature followed by replacement of H_2 by D_2 . After 1 hr at -25°C the amount and ratio of diastereomers of **5** showed no change, but upon warming to room temperature the hydride resonances rapidly diminished and disappeared within 1 hr, following first order kinetics with a rate constant of $3.3 \times 10^{-3} \text{ s}^{-1}$ for diastereomer **5a**.

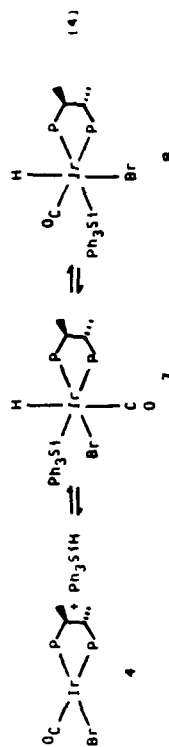
The experiments outlined above show that in addition to the stereoselective, kinetically-controlled H_2 oxidative addition originally seen in eqn (1), diastereoselection for **5** and **6** occurs due solely to the influence of chiraphos on the developing chirality at the metal center as the *cis* oxidative addition proceeds. The kinetic differentiation expressed as $\Delta\Delta G^\ddagger$ for **5a:5b** and **6a:6b** is 0.40 and 0.50 kcal/mole, respectively. From the experiment under D_2 , we see that reductive elimination of H_2 from **5** is rapid at room temperature, indicating that equilibrium between **5a** and **5b** is established prior to isomerization to **6**, and suggesting that the mechanism for isomerization involves reductive elimination to generate **4** followed by oxidative addition with H_2 parallel to **P-Ir-X** forming **6**. The proposed mechanism is shown as eqn (2),⁶ from the initially observed ratio of >200:1 for **5:6** and eqn (3), we conclude that $\Delta\Delta G^\ddagger$ between the formation of **5a** and **6a** must be >3.1 kcal/mole. The thermodynamic differentiation between



the diastereomers is obtained from the ratio of **5a:5b** as **6** starts to form, and the ratios **6a:6b** and **6a:5a** after equilibrium has been reached. A

reaction coordinate profile of the $4 + \text{H}_2$ system summarizing all of these results is given in Figure 2.

The oxidative addition of Ph_3SiH to **4** also proceeds stereoselectively under kinetic control in agreement with recent observations for silane addition to complex 1.⁷ The reaction occurs as shown in eqn (4) with the initial formation of **7** (>99.5%) followed by isomerization to the more stable diastereomers **8:8**. The kinetic differentiation for **8** is striking as evidenced by the ratio for **8a:8b** of 12:1 during early stages of the isomerization, corresponding to $\Delta\Delta G^\ddagger$ of 1.5 kcal/mole for the formation of the diastereomers. The eventual ratio of **8a:8b** at equilibrium is 1:1 indicating little thermodynamic differentiation between the diastereomers.



The isomerization of 7 to 8 most probably occurs by reductive

elimination/oxidative addition similar to that shown in (2) since the reaction follows first order kinetics and reductive elimination of Ph_3SiH from 7 is rapid relative to isomerization. The latter was shown by preparing 7 at -20°C followed by the addition of 5 eq MeCl_2SiH which acts as an efficient trap for 4 by its oxidative addition to form $\text{IrH}(\text{SiMeCl}_2)_2(\text{CO})(\text{chiraphos})$. Further studies using these and other silanes will be reported separately.

The results described above show that kinetic and thermodynamic differentiation of metal centered chirality in simple cis oxidative additions of chiraphos is significant.⁹ The results also provide a sensitive probe to the transition state structure in these systems through observed differences in the extent of kinetic and thermodynamic differentiation for the diastereomers in these cis oxidative additions. Based on these differences, it appears that for both H_2 and Ph_3SiH oxidative addition, the transition state in these reactions is not very product like.

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5. ^1H NMR data for hydride resonances in d_6 -acetone (J_{PH} in Hz). 5a: -8.85 (dd; 144.7, 12.9), -9.25 (dd; 21.6, 16.7). 5b: -9.02 (dd; 145.9, 12.9), -9.28 (-t; 20.8). 6a: -8.71 (ddd; 127.1, 15.7, 4.3), -18.0 (mult). 6b: -9.50 (ddd; 128.8, 16.7, 4.9), -18.1 (mult).

- The assignment of metal-centered chirality for all of the diastereomers is based on an analysis of space-filling models of reactants and products for the oxidative addition reaction. These models, which are particularly informative for the silane oxidative addition, predict a kinetic preference for the Δ configuration in the formation of both 5 and 6, and little thermodynamic differentiation within each pair of diastereomers. These predictions must, of course, be confirmed by x-ray structural studies. A different analysis has been presented by Brown and Chaloner who propose that diastereoselection of H_2 oxidative addition to $\text{Rh}(\alpha\text{-benzamido}(\text{acido})\text{chiraphos})^+$, which was not observed directly, is determined by torsional strain in the Rh-chiraphos chelate ring. Brown, J. M.; Chaloner, P. A. in "Homogeneous Catalysis with Metal Phosphine Complexes", L. Pignolet, Ed., Plenum Publishing, New York, **1983**, 161-2. However, the importance of electronic factors in determining the diastereoselection in the $\text{Rh}(\text{chiraphos})$ system has not been examined as it has for $\text{IrBr}(\text{CO})(\text{dppe})$.

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8. ^1H NMR data for hydride resonances in d_6 acetone (δ ppm in Hz). 7a: -7.9J (dd, 16.8, 12.6). 7b: 8.49 (dd, 24.2, 13.7). 8a: -16.04 (dd, 13.7, 7.4). 8b: 16.14 (dd, 24.2, 5.3). Molecular models indicate that the configuration at the metal for diastereomer 8a which is kinetically preferred over 8b is 4.
9. a. While diastereomeric cis dihydrides have been seen previously for $(\text{C}_6\text{H}_5)_2(\text{diphenyl})\text{IrF}_4$, the stereoselectivity of the oxidative addition was not reported. Brown, J. M.; Day, F. M.; Lightowler, D. J. Chem. Soc., Chem. Commun. 1983, 414. b. for the oxidative addition of H_2 to $[\text{Ir}(\text{cod})\text{diop}]\text{PF}_6$, only one set of hydride resonances was discernable. Presumably the diastereomers were not resolved. Crabtree, R. M.; Felkin, M.; Filibeau-Khan, T.; Morris, G. E. J. Organomet. Chem. 1979, 168, 183.

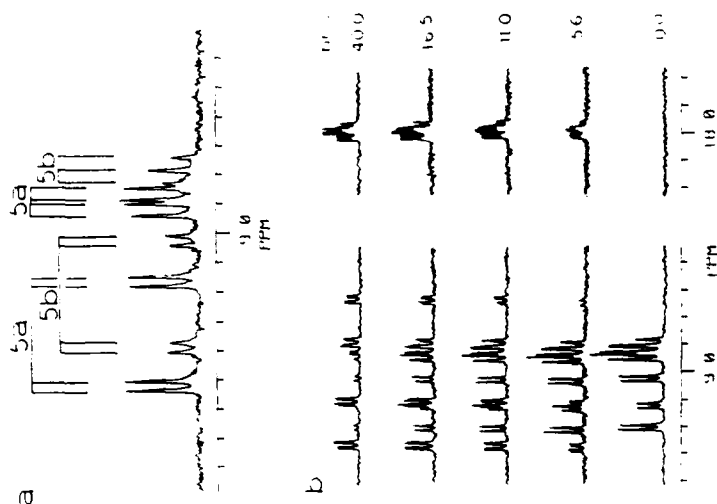


Figure 1. Hydride region of the ^1H NMR spectrum of $\text{IrBr}(\text{CO})(\text{chiraphos})$, 4, plus H_2 in d_6 -acetone: (a) expanded view at -25°C ; (b) spectra taken over 40 hr period monitoring the conversion from diastereomers 5 to 6 at 25°C .

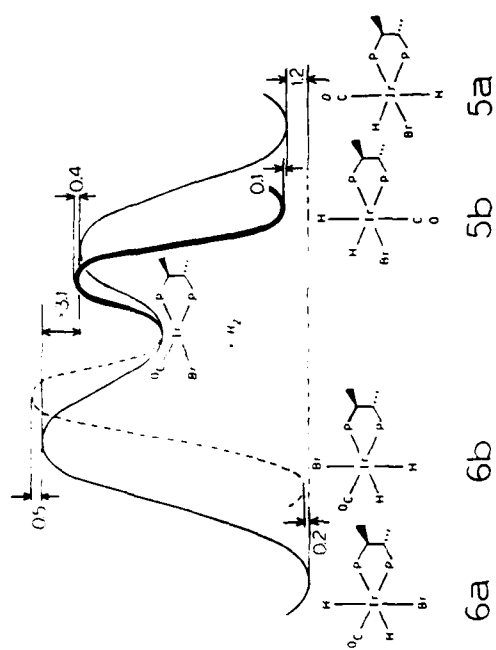


Figure 2. Reaction coordinate diagram for the system $\text{IrBr(CO)(chiraphos)}, 4$, + H_2 . Values of $\Delta\Delta G^\ddagger$ and $\Delta\Delta G^\circ$ are given in kcal/mole.

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